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A review on process conditions for optimum bio-oil yield in hydrothermal liquefaction of biomass

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ABSTRACT

Hydrothermal liquefaction is a technique for obtaining clean biofuel from biomass in the presence of a solvent at moderate to high temperature (250–550 °C) and pressure (5–25 MPa). Hydrothermal decomposition of biomass leads to the formation of various compounds depending upon operating parameters. The role of processing conditions including final liquefaction temperature, residence times, rate of biomass heating, size of biomass particles, type of solvent media and hydrogen donor solvents is important for the bio-oil yield and quality of the product. The effect of these parameters on the yield and composition of the liquid products is reviewed in the paper. A brief description about the decomposition mechanism is also included to highlight the product types during hydrothermal liquefaction.

Contents

1. Introduction

Biomass is a biological matter, which includes both fauna and flora. Biomass resources include wood and wood waste, energy crops, aquatic plants, agricultural crops, and animal wastes. Municipal and milling activities generate huge quantities of mixed biomass like sawdust, manure, sewage sludge, cooking wastes. Vegetative biomass is generally composed of lignin, cellulose, and hemicelluloses and varies in composition depending on plant species. Both cellulose and lignin exhibit the plenteous carbon reproducibility on earth. Cellulose is a linear polymer of glucopyranose with molecular weight >100,000. Lignin is an amorphous phenolic polymer, which builds on p-hydroxyphenylpropane, guaiacylpropane, and syringylpropane monomers. Mannose, glucose, and xylose polymerize to hemicelluloses. Lignin and hemicelluloses are components of cell wall to provide necessary rigidity and are often called lignocelluloses [1–3].

Biomass can broadly be categorized as organic matters build up by plants during photosynthesis in which sunlight and CO_2 is converted into chemical energy leading to cellulosic biomass

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such as.

$$6CO_2 + 5H_2O \overset{\text{sunglight}}{\longrightarrow} C_6H_{10}O_5 + 6O_2 \quad (1)$$

The bio-energy thus produced by plants is amassed in flora as biomass energy. During combustion of biomass, the same amount of heat energy and carbon dioxide is produced. It essence biomass as renewable energy source that can share fossil energy loads.

Over the years, fossil fuels have been the cheapest source for petroleum and petrochemical industries, which led to the development of millions of petroleum based products. However, fuel price demand has reached record hikes in recent times triggered by factors like depletion of easily accessible deposits, ever increasing demand by emerging economies. The increase in energy demand requires replacement of a major portion of the fuel with green energy supplies and technological development for the said purpose [3]. Steady decline in valuable petroleum commodity against ever-increasing demand has drove researchers to search for alternative resources for energy and chemicals. Biomass may likely be the solution to the search [4]. Biomass was once the global major energy source before the advent of fossil fuels. Fossil energy being the cheapest and easily accessible, dominated all other energy resources over the recent past. However, fossil oil depletion and its uneconomical extraction have once again highlighted biomass as a source of energy in transportation and power generation related applications. Huge potential also lies in production of various chemical products from biomass that can serve humanity at cheaper price than petroleum based chemicals (petrochemicals). Being a renewable source, biomass can carry the energy loads demand worldwide. Environmental and social issues are other triggers for biomass utilization, which can boost clean environment and social well-being of less developed areas. Certain advantages in utilizing biomass as an alternative energy include: (i) CO_2 free substitute of fossil fuel, (ii) SO_x, NO_x trimmer, (iii) biodiversity and social prospects. Plants consume carbon dioxide during photosynthesis, which helps to reduce greenhouse gases (GHG). By maintaining a balance between plant biomass production and its utilization, it is possible to achieve almost zero GHG emissions. CO_2 emissions on g/KWh electricity generation bases are the lowest in case of biomass (17–27) compared to coal (955), oil (818) and gas (446). With improved biomass utilization technology in future, biomass is expected to emit only 15–18 g/KWh of CO_2 supporting its CO_2 neutral nature [5].

The present scenario in alternative energy demonstrates renewable energy has great potentials and research activities have focused to economically utilize abundant biomass to benefit humanity. However, millions of tones of biomass globally produced every year is either used in domestic and low level commercial activities or degraded by microorganisms. For example in the United States, out of 512 millions tones of biomass produced in 2004 only 15% was used as fuel [4]. Biomass conversion into fuels and chemicals can save foreign reserves and boost economic activity in regions of the world, which lack in fossil fuel resources and have abundant biomass such as Malaysia, Thailand, and Indonesia. Conversion of biomass into fuels and chemicals can share demand loads of such commodities in order to avail cheaper means of transportation, electricity, and chemicals like bio-plastics, bio-fertilizers, and bio-polyesters. Conversion of waste biomass would also reduce dumping costs such as in incineration of municipal wastes diminishing up to 90% wastes volume and producing fuels or biomass based chemicals [6]. Technology that can base such utilizations would propel research, social and economical activities and would decrease reliance on fossil energy. Thus, share of biomass energy to meet world energy demand is expected to rise in future boosting technological development for biomass utilization. The major objective of this review is to summarize the effect of processing parameters on hydrothermal liquefaction yield. Scattered information about processing parameters has been discussed in original articles, technical notes, and review papers. This review is an effort to elucidate the role of operating conditions on bio-oil yields and compositions. Besides, a brief detail about mechanistic aspects is also included to examine the relationship between processing parameters and oil yield in hydrothermal media.

2. Hydrothermal extraction of biomass

Water present in biomass poses negative effect on pyrolysis, as it requires high heat of vaporization. This limits the options for biomass as feedstock and overall process economy. In general, pyrolytic liquefaction usually liquefies biomass suitably having <40% of moisture contents. Water contents in tropical grasses can be as high as 80–85% or similarly ∼90% for aquatic species. Biomass usually requires preprocessing to suit for pyrolysis applications. In order to cater moisture content problem, few studies have suggested atmospheric drying followed by mechanical dehydration [7]. Nevertheless, other means of drying has also been applied [8]. Solar drying may be cost effective but it requires longer times for biomass to lower the moisture contents. Other dehydration methods are costly and make pyrolysis processes uneconomical. One solution to handle high moisture contents in biomass can be hydrothermal liquefaction of biomass. This method can liquefy biomass with any level of moisture contents. Hydrothermal liquefaction yields high biomass conversion and relatively pure products. Biomass like grasses, tropical and aquatic plantations can suitably be liquefied by hydrothermal extraction process. Fluids possess high salvation power at hydrothermal conditions. Under hydrothermal conditions, fluids attain properties suitable for biomass liquefaction such as high density, good heat, and mass transfer capabilities like in gases, fast decomposition, and extraction [9,10]. However, under extreme operating conditions, corrosion and scaling are major limitations of sub/supercritical fluids operations.

Hydrothermal liquefaction is an environment friendly technology. Unlike the hazardous products of combustion, such as ammonia, NO_x, etc, hydrothermal oxidation converts heteroatom's present in biomass are converted into harmless byproducts. Under hydrothermal water conditions, biomass and oxygen rapidly oxidize or mineralize to form CO_2 or H_2O. Nitrogen heteroatom present in biomass, mainly converts N_2 with some N_2O. Sulfur, chlorine, and phosphorous are mainly oxidized to their respective inorganic acids that are neutralized to salt by adding suitable base [11]. However, the presence of acids during hydrothermal processing can harm vessel lining and require some precautionary measures. Addition of weak base along with biomass in SCWO may inhibit the corrosive action of acids. Hydrothermal oxidation is an effective proven technology suitable for wide range of feedstock including wet biomass, sewage sludge, and high sulfur coals. A review of previous studies on different type of biomass using sub/supercritical oxidation is shown in Table 1. Excellent reviews for hydrothermal liquefaction of can be referred for further information [11–19].

3. Effect of processing parameters on bio oil yield during hydrothermal biomass liquefaction

3.1. Effect of temperature

Generally, it is accepted that temperature adds synergetic effect on the yield of liquids due to extended biomass fragmentations with increase in temperature. When the temperature is sufficiently larger than the activation energies for the bond cessation, the extensive biomass depolymerization occurs. This increases both

Table 1
shows the effect of solvent types and operating conditions on the liquid oil yield.

Biomass type	Solvent type	T_c (K)	% bio-liquid yield	Ref.
Prang mites australis	Ethanol	516	53.6	[20]
	Methanol	513	38.7	
Cotton cocoon shell	Acetone	508	35.6	[21]
	Water	653	69.1	
Corncob	Water	575	75	[10]
Verbascum stalk	Methanol	573	60.5	[22]
	Ethanol	573	43.3	
	Water	647.8	17.1	
Rice straw	Ethanol–water (5:5)	573	38.35	[23]
	2-Propanol–water (5:5)	573	39.7	

concentration of free radicals and probability of repolymerization of fragmented species. The competition among hydrolysis, fragmentation and repolymerization reactions defines the role of temperature during pyrolysis. Depolymerization of biomass is a dominant reaction during initial stages of pyrolysis. Repolymerization becomes active at later stages that leads to the formation of char. Intermediate temperature usually yields higher amounts of bio oil. The suitable temperature for production of oil yield also depends upon biomass types which is discussed later in this review. Selection of optimum temperature can be a task as properties of water changes rapidly in near supercritical conditions. The temperature higher than 374 °C supports greatly to the gas formation [24]. Karagoz et al. [25] reported the liquefaction of sawdust at 180 °C, 250 °C and 280 °C. The total oil yield at these temperatures was 3.7%, 7.6% and 8.5% respectively – indicating the synergetic effect of temperature increase on sawdust liquefaction. Maximum of 45% water solubles were produced at 250 °C possibly due to decomposition of cellulose around this temperature [26]. Xu and Etcheverry [27] reported the effect of sub- and supercritical conditions on liquefaction of Jack pine powder in H_2 environment. Under 2.0 MPa pressure of H_2, temperature shift from subcritical (220 °C) to near supercritical (350 °C) observed 25% increase in oil yield. Rate of liquids production was higher from temperature range 250 °C to 300 °C. Decrease in sawdust degradation rate around 300 °C was attributed to repolymerization and cyclization of fragments. Liquefaction is thermodynamically unfavorable since at low temperatures biomass liquefaction is endothermic, but exothermic at high temperatures.

Influence of temperature on the yield of liquefaction products seems sequential. Initially the rise in temperature triggers bio-oil yield. After reaching a maxima for the oil yield, further increase in temperature actually inhibits biomass liquefaction. Very high temperature is not usually suitable for production of liquid oils both in terms of operational cost and liquid oil yield. In general, there are two reasons for this behavior. Firstly the secondary decompositions and Bourdard gas reactions become active at high temperatures which lead to the formation of gases [28]. Secondly, the recombination of free radical reactions leads to the char formation due to their high concentrations. These two mechanisms become dominant at high temperatures, which reduce the production of oil from biomass. Moreover, at temperatures <280 °C, incomplete decomposition of individual biomass components suppresses the bio oil yield. Under hydrothermal conditions, lignin and cellulose fragments rapidly at >250 °C [29]. Thus, it can be presumed that 300–350 °C would be an effective temperature range for decomposition of biomass both for sub- and supercritical conditions.

Fig. 1 gives information on variation in yield of liquid oil produced from biomass as a function of temperature in hydrothermal media. Liquefaction at low temperature produced insignificant amount of liquid oils. According to studies by Zhou et al. [30], Yin et al. [31], Zhang et al. [32], and Sugano et al. [33], temperature range of 300–315 °C was suitable for efficient production of liquid oils. Biomass feedstocks used by them were *Enteromorpha prolifa*, *cattle manure*, *grassland perennials* and *eucalyptus*, respectively. These biomass types are similar to each other and are loosely structured. Similar results were reported in Qu et al. [34] for liquefaction of *Cunninghamia lanceolata*. High yield of liquid oils approximately 76% at 300–310 °C reported in Zhang et al. [32] are due to the fact that they supposed acetone solubles as liquid oil fraction. So in their case, liquid oil fraction included both acetone and bio oil. These study highlighted that final temperature range of 300–330 °C was sufficient for production of bio-oil. All of the biomass used in these studies can be regarded grasses or softwood species. This may indicate that biomass type can effect the final temperature of liquefaction. Xiu et al. [35] observed that increasing temperature from 260 to 340 °C increased the amount of bio oil from liquefaction of manure. However, Shuping et al. [37] liquefied microalgae *Dunaliella tertiolecta* cake and observed ∼360 °C as optimum temperature. The useful temperature range for hydrothermal liquefaction can range from 300 to 350 °C. According to Fig. 2, the amount of solid residue sharply decreased as function of temperature for liquefaction of lignocelluloses biomass (eucalyptus). The amount of solid residue was ∼14 wt% at 300 °C and there was negligible decrease afterwards. At the same time maximum amount of liquids oils were obtained at 300 °C. This showed that variations in the amount of solid residue can be set as reference point to measure optimum liquefaction temperature. Suggestable temperature for hydrothermal liquefaction can be sought around 300 °C. However, in compact biomass types may require higher temperature.

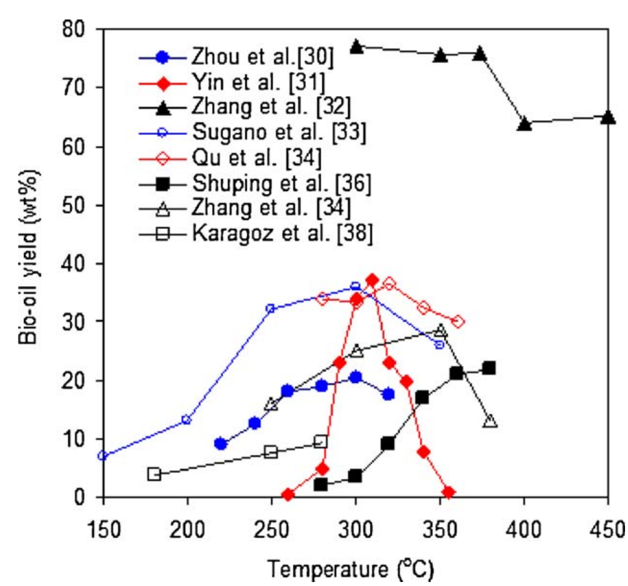


Fig. 1. Effect of temperature on yield of liquid oils.

Table 2
Effect of feedstock types on the composition of bio oil by hydrothermal process.

Feedstock type	Bio oil composition	Temp. (K)	Ref.
Monosaccharide (glucose, mannose, fructose, galactose, D-sorbitol)	5-Hydroxymethylfurfural, 2-furaldehyde glycolaldehyde, dihydroxyacetone glyceraldehydes, 1,2,4-benzenetriol pyruvaldehyde, lactic acid, acrylic acid acetaldehyde, formic acid, acetic acid glycolic acid, acetone	613	[41]
Cellulose	Acids, cellibiose, erythrose, 1-6 anhydroglucose, 5HMF	623	[42]
Catechol	Cyclopentanone, 5-hydroxymethylfuran, 2-methyl-2-cyclopentenone, phenoxymethane, 3-methyl-2-cyclopentenone, phenol, octamethyltetrasiloxane, *o*-cresol methyl ether, cymene, 2-cyclopenten-1-one, 2,3-dimethyl, *o*-cresol, *p*-guaiacol, *m*-cresol, guaiacol, 2-methylindane, methyl guaiacol, cyclopentasiloxane, *p*-cresol, catechol, *p*-methylguaiacol, 2-formyl-4-methoxyphenoll, *p*-ethylguaiacol 2,5-dimethoxytoluene, dodecamethylcyclohexasiloxane, 1,3-bis(trimethylsiloxy) benzene, 3-isopropylbenzaldehyde, 1-hydroxy-4-aminoanthraquinone, methylisopropylphenanthrene	623	[43]

3.2. *Effect of particle size*

The purpose of particle size reduction is to increase the accessibility of biomass to hydrothermal treatment for achieving higher degree of hydrolysis and fragmentation. It is also true that size reduction of biomass costs considerable amount of energy. Thus, an optimum particle size of biomass should increase the yield of products of hydrothermal liquefaction at low grinding cost. In general, particle size imparts negligible to low effects in hydrothermal liquefaction of biomass. This is because sub/supercritical water act both as a heat transfer medium and as an extractant. Sub-/supercritical water help to overcome the heat transfer limitations in hydrothermal liquefaction, which makes particle size as a secondary parameter. Hydrothermal liquefaction is relatively insensitive to size of the particle and there is no need for excessive size reduction of biomass feedstock. Zhang et al. [32] observed the effect of three different particles sizes (1 in, 2 mm and 0.5 mm) on the liquid oil yield in hydrothermal liquefaction of grass perennials. According to their observations particle size reduction did not improve the liquid oil yield at 350 °C. There was 2% reduction in the yield of liquid oils at supercritical conditions (374 °C, 22.1 MPa). Effect of particle size on product distributions is not widely discussed in literature due to its low importance as parameter. The particle size distributions that lead to the low grinding costs are usually recommendable. Coarse grinding leads to low energy consumption while fine grinding requires large energy inputs with little increase in surface area. According to Mani et al. [39], grinding cost was almost double for particle size reduction from 3.2 mm to 0.8 mm during dry grinding of wheat straw, barley straw, and switch grass. For hydrothermal liquefaction purposes, the particle size in between 4 and 10 mm will be suitable to overcome heat and mass transfer limitations at reasonable grinding cost.

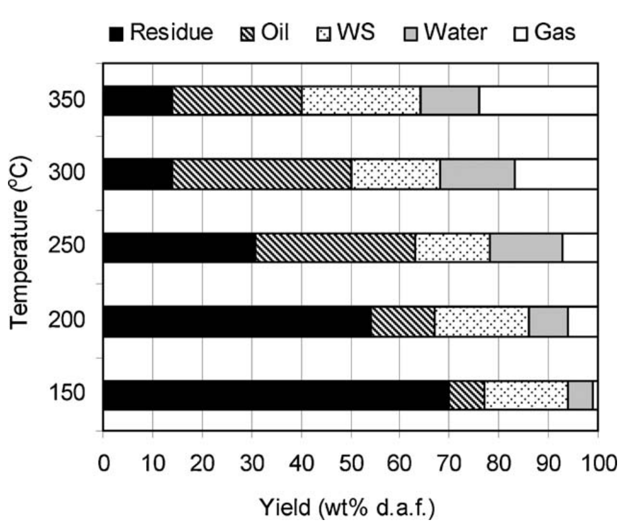


Fig. 2. Yield of liquefaction products as function of temperature Sugano et al. [33].

3.3. *Effect of biomass feedstock*

Heterogeneity in biomass stock leads to the modification in liquid products and overall yield. This is because major biomass components such as lignin, hemicelluloses, and cellulose behave differently to hydrothermal temperature variations. In general, presence of high cellulose and hemicelluloses content in biomass yields more bio-oil. For example, hardwood samples (cherry) produced more oils than softwood (cypress) due to the high lignin contents in later biomass [40]. Zhong and Wei [24] studied the effect of temperature on aqueous liquefaction of four different woods (*C. lanceolata*, *Fraxinus mandshurica*, *Pinus massoniana* Lamb. and *Populus tomentosa* Carr.). Bio-oil yield was influenced by both temperature and lignin contents of wood. Heavy oil production was the maximum for Fraxinus mandsurica wood type due to its low lignin contents. Even at high temperature (>330), cyclization and repolymerization of lignin fragments of liquid oil reduced oil yield [10]. Lignin is difficult to degrade and mostly appears in residue fraction. Eqs. (2) and (3) provide a correlation between char residue amount and lignin contents of wood biomass under operating conditions described in [24].

$$\text{maximum heavy oil yield} = 40.525 - 0.583 \times (\text{lignin percentage}) \quad (2)$$

$$\text{maximum amount of char residue} = \text{lignin percentage} - 5.477 \quad (3)$$

The final pyrolysis temperature to produce maximum oil yield also tends to increase with lignin contents in biomass. For example, a presence of 32.44% lignin in *C. lanceolata* wood sample shifted the final pyrolysis temperature to 613 K compared to 573 K in case of *Fraxinum madshuria* wood (21% lignin) [24]. Thus, it is presumable that presence of lignin in biomass leads to low oil fractions during pyrolysis. On the other hand, hydrothermal decomposition of both the cellulose and hemicelluloses enhances the aqueous fraction. The decomposition potential for individual biomass component owes to their structure. Decomposition is easier in hemicelluloses due to amorphous structure. Cellulose is little crystalline to decompose due to β (1-4) glucosidic linkages and relatively intermediate

degree of polymerization (500–10,000). High degree of polymerization (>10,000) and complex branching makes lignin difficult to decompose even at very high temperature [11]. Physical properties of bio-oil also depend upon the feedstock type. Oxygen and moisture contents are usually high in bio oil obtained from liquefaction of loosely structured biomass species. This significantly lowers the oil quality and HHV. The viscosity is also low in such species. The reverse is true for compact biomass such as coal.

Finally, the variations in the bio oil composition also depend upon the biomass feedstock. This is due to the differences in the building blocks of three major components of lignocellulosic biomass. Hydrothermal decomposition of cellulose and hemicelluloses lead to the formation of sugars and aqueous decomposition products. Major products of hollocelluloses degradation include cellohexaose, cellopentaose, cellotriose, cellobiose, fructose, glucose, erythrose, glycolaldehyde, glyceraldehydes, pyruvaldehyde, and furfurals. Table 2 shows the effect of different biomass feedstock on the composition of oil obtained in hydrothermal liquefaction.

3.4. Effect of biomass heating rate

Higher heating rates are supportive for bulk fragmentation of biomass and inhibit the char formation. This is true for both pyrolysis and hydrothermal liquefaction of biomass. However, heating rates impart low effect on the product distributions in hydrothermal liquefaction than in pyrolysis. The reason to this point is the better dissolution and stabilization of fragmented species in hot compressed water (solvent) medium. Even in pyrolysis, the presence of moisture contents resists char formation and improves liquid oil yield [44]. Zhang et al. [32] observed synergetic effect of heat up rates on the yield of liquid oils during hydrothermal liquefaction of grassland perennials. For heating rates interval of 5–140 °C/min, liquid oil yield increased from 63% to 76%. For practical purposes, empirical correlation may be suitable to estimate the yield of liquid oil, as a function of heating rates as shown in Eq. (4). Design of experiments and regression analysis are helpful to develop an equation for particular biomass species and operating conditions [32].

$$\text{liquid yield}(\%) = [0.0042 \times \ln(\text{heating rate}) + 0.5514] \times 100 \quad (4)$$

Slow heating rates usually lead to the formation of char residue due to secondary reactions. Secondary reactions become also dominant at very high heating rates which results in high gas yields as in case of supercritical liquefaction. Moreover, liquid oil yield is not very sensitive to large variations in high heating rates. Suitable heating rates can lead extensive fragmentation and minimal secondary reactions. On such bases, moderate heating rates may be enough to overcome heat transfer limitations and to produce high liquid oil amounts.

3.5. Effect of solvent density

Many researchers have investigated the potential effect of water or solvent density on liquefaction yield of hydrothermal processes [25,43,44]. Mass ratio of biomass to water is considered a key parameter. In general, high amount of water is suitable for production of liquids and gas yield, possibly due to enhanced extraction by denser solvent medium [45]. Wang et al. [46] observed that high solvent to mass ratios reduced the amount of leftover residues. This reduction can be attributed to increase in salvation for biomass components. Apart from residues reduction, high amounts of solvents also decreased gas yield [47]. For comparison, pyrolysis of biomass usually produced more gases than hydrothermal liquefaction [25]. This suggested that solvents enhance the stability and solubility of fragmented components. During hydrothermal treatment of biomass, solvents extract the biomass components that enhance the dissolution of biomass fragments. At high biomass to water ratios, the relative interactions among molecules of biomass and that of water become less influential, which can suppress dissolution of biomass components. Hydrothermal process tends to behave like pyrolysis at very high biomass to solvent ratios. However, increasing biomass to water ratio does not always yield high liquid amounts. Bookcock and Sherman [47] observed that at very low biomass/solvent ratios, the amount of liquid oils decreased comprehensively.

3.6. Effect of pressure

Pressure is another parameter for degradation of biomass in hydrothermal liquefactions. Pressure maintains single-phase media for both sub- and supercritical liquefactions. This single-phase liquefaction is necessary to avoid large enthalpy inputs required for phase change of solvents. Two-phase system requires large heat supply to maintain the temperature of the system [48]. By maintaining pressure above the critical pressure of medium, the rate of hydrolysis and biomass dissolution can be controlled that may enhance favorable reaction pathways thermodynamically for production of liquid fuels or for gas yield. Pressure also increases solvent density. High-density medium penetrates efficiently into molecules of biomass components, which results in enhanced decomposition and extraction [49]. However, once supercritical conditions for liquefaction are achieved, pressure impart little or negligible influence on yield of liquid oil or gas yield [50–53]. This is because in supercritical region, influence of pressure on the properties of water or solvent medium is very small. Sangon et al. [50] observed that increase in pressure (7–12 MPa) slightly increased liquefied oil yield during coal liquefaction in supercritical conditions. Catalytic runs in the same study actually decreased the amount of oil with increase in pressure, which can be attributed to blocking of catalyst active sites by high-density solvent. Kabyemela et al. [53] observed that rate constant for glucose degradation was lowered by pressure rise. Kabyemela et al. [52] reported that pressure change (30–40 MPa) at 400 °C could not influence the rate of hydrolysis for cellobiose liquefaction and observed the decrease in rate of pyrolysis of the same. Pyrolysis of biomass depends upon breakage of C–C linkages. However, when pressure is increased in supercritical conditions, the increase in local solvent density causes cage effect for these bonds. This cage effect inhibits C–C bonds breakage, which ends up in low fragmentations. Thus, variation of pressure in supercritical liquefaction may not play an important role for overall liquid oil yields.

3.7. Effect of residence times

Many researchers have investigated effect of residence times on hydrothermal liquefaction [34,54–57]. Duration of reaction times may define the composition of products and overall conversion of biomass. As rate of hydrolysis and decomposition is relatively fast in supercritical processes [58], the short residence times are expected to degrade biomass effectively. Normally in supercritical water oxidation waste treatments, dilute organic compounds are destroyed by oxidants at supercritical temperature and pressure for short residence times. However, optimization of residence times is necessary for effective destruction of organic compounds in biomass [59]. During hydrothermal biomass liquefaction, small residence times are usually preferred as well. Different studies have reported results for bio-oil yield as a function of residence time. According to Boocock and Sherman [47], longer residence times suppressed the bio-oil yield except for very high biomass to water ratios. Yan et al. [57] observed negligible increase in liquid yields for longer

residence times on liquid yields. Karagoz et al. [38] reported that increase in residence times at low temperatures (150 °C) favored the liquid oil yield and conversion of sawdust. Reverse was true for high temperatures (250–280 °C) although overall conversion of biomass and gas yield increased with rise in temperature. Qu et al. [33] observed decrease in heavy oil yield for longer residence times and concluded that shorter residence times produced more amount of oil. There may be many reasons to the effect of residence times in liquefaction. In hydrothermal medium, there are always chances for the secondary and tertiary reactions. These reactions can convert heavy intermediates either into liquids, gases, or residues species. Once conversion of biomass reached its saturation point, the chances for decrease in oil yields become even more probable. Residence times may also affect the composition of bio oil. According to Karagoz et al. [38], the decomposition products were not similar for longer and shorter residences times both for low (180 °C) and high (250 °C) temperatures. For example, 5-(hydroxymethyl)-2-furan carboxaldehyde, 4-hydroxy-3-methoxybenzoic acid, 4-hydroxy-3-methoxybenzeneacetic acid and bis-(2-ethylyhexyl) phthalate were observed for 60 min, which could not be found in short residence times cases (15 min). It is also notable that longer times can decompose preasphaltenes and asphaltene into lighter products, which can enhance the yield of light oil and gases [47]. To obtain high liquid oil yield, it is necessary to inhibit the decomposition of lighter products. Addition of reducing agents like tetraline, hydrogen, and syngas can stabilize the radicals and products. In general, oil yield reaches a maximum before decreasing for very long residence times while gas yield and biomass conversion increase continuously until the saturation point [55].

3.8. Effect of reducing gas/hydrogen donors

The role of reducing gases or for hydrogen donors is to stabilize the fragmented products of liquefaction. Reducing species inhibit the condensation, cyclization, or re-polymerization of free radicals, and hence reduce char formation [27]. Eqs. (5) and (6) show the concept for stabilization of aromatic radicals ($Ar^{\bullet}$) of lignin by hydrogen gas to useful liquid oil products [36]. Although H_2 is very effective in stabilizing the fragmented products, it is a costly option. Alternatively, synthesis gas (CO/H_2), steam, N_2 and Argon, etc. are other options to serve the same purpose.

$$Ar^{\bullet} + H_2 \rightarrow ArH + H^{\bullet} \quad (5)$$

$$Ar^{\bullet} + H^{\bullet} \rightarrow ArH \quad (6)$$

According to Fig. 3 bio oil yield peaked at 310 °C irrespective of the reducing environment. However, reducing gases influenced the overall yield of bio oil during the hydrothermal processing of cattle manure. This probably may be due to the different reactivity of the reducing gases. Air cannot be used as reducing gas since it leads to the combustion of the biomass. That is why; the amount of bio oil yield was considerably lower at all temperature points studied. Results showed that higher reactivity of CO and H_2 stabilized more of fragmented radicals during liquefaction. Probably biomass radicals show more affinity of towards H_2 or CO and get stabilize easily. Less amount liquid oils in N_2 environment is mainly due to its low reactivity comparatively. This discussion shows us that reactive gases are better options for hydrothermal liquefaction than inert gases. H_2 gas or mixture of CO/H_2 gases is recommendable as reducing gases. Usage CO as reducing gas may be ignored due to its hazardous nature.

Bubbling nature of reducing gases require specialized pyrolyzers to inhibit both the gas channeling and its maldistribution. To offset these problems, hydrogen donor (HD) solvents are the more favorable option to hydrogenate the biomass fragments compared to reducing gases. These solvents not only donate hydrogen but

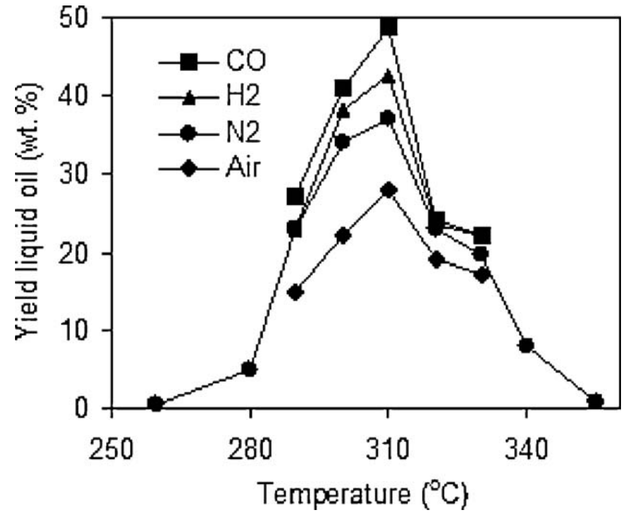
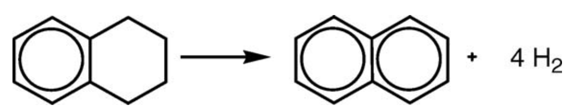


Fig. 3. Effect of reducing gases on liquid oil yield as a function of liquefaction temperature Yin et al. [31].

also act as hydrogen transport vehicle [60]. Ability of a HD solvent to release hydrogen defines its hydrogenation power. Tetralin is among the popular solvents for hydrogenation of fragmented species. Tetrahydrophenanthrene, octahydrophenanthrene, hexahydropyrene, hexahydrofluorene, and tetrahydroacenaphthene are other useful solvents for hydrogenation. Eq. (7) shows the release of hydrogen atoms by a hydroaromatic compound [61].



(7)

Many researchers have elucidated the effect of hydrogen donor species on the composition of products of liquefaction. Wang et al. [60] observed the effect of solvents and reducing gases on the yield of liquids, gases, asphaltenes, and preasphaletes in liquefaction of sawdust. Presence of tetralin solvent enhanced liquid oil yield by suppressing the formation of asphaltenes, preasphaltenes and gases. Tetralin produced 58.9% liquids compared to 42% for toluene solvent (non-hydrogen donor). Reducing gases (H_2 or syngas) favored the formation of gases and suppressed liquid oils <40%. It is noticeable in this study, that high yield of liquid in case of tetralin solvent is due to suppressed asphaltenes, preasphaltenes or gases. This is because of the hydrogen shuttling ability of HD solvents, which overcome hydrogen distribution and mass transfer limitations. Prompt supply of hydrogen enhances the hydrogenation reactions among asphaltenes, and preasphaltenes and inhibits their poly-condensation. Dissolution effect of HD solvents stabilizes gases quickly before these can actually escape from the decomposing matrix. Moreover, HD solvents donate hydrogen to separate oxygen contents from major biomass constituents by facilitating water formation. This increases the HHV of bio oil and thus its quality [62]. Reducing gases only impart secondary effect on the yield of liquids. Irrespective of the fact that reducing gases can modify the composition of products of liquefaction, such gases only add negligible to low effect. Boocock and Sherman [47] observed negligible effect of hydrogen or nitrogen gases on the products composition of wood hydropyrolysis. Similarly, Xu and Etcheverry [27], and Bestue-Labazuy et al. [63] also suggest the low effect of hydrogen gas on products of liquefaction. However, addition of a suitable catalyst markedly enhances the effectiveness of reducing gas [60,64]. A formal interaction among the molecules of reducing gas and fragmented species of biomass is necessary for stabilization of such fragments. Low probability of reactions among the

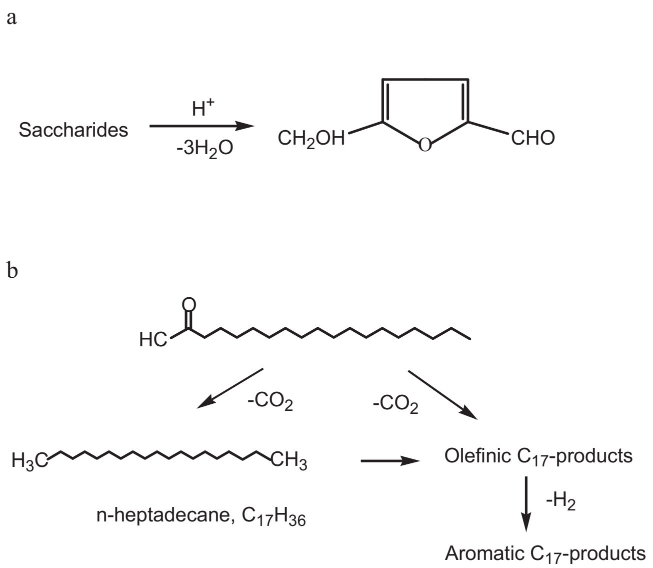


Fig. 4. (a) Dehydration of saccharides to 5-hydroxymethylfurfural [70]. (b) Simplified decarboxylation network of stearic acid to diesel products [71].

reducing gas molecules and free radicals leads to the high gas or char yield possibly due to high condensation and rearrangement of free radicals. Adsorption of reducing gas on a catalyst surface may increase probability of reactions among the species. This can be the possible explanation for the increase in liquid oil yield by catalyst/reducing gas combination. Table 3 shows the effect of HD solvents and reducing gas on the yield of products of liquefaction.

4. Brief description on decomposition mechanism in hydrothermal liquefaction

One of the main purposes of biomass liquefaction processes is to decrease oxygen contents of biomass. In general, oxygen represents 40–50% of the wood biomass. Dehydration and decarboxylation are two major reactions that can remove oxygen heteroatom in the form of H_2O and CO_2 respectively. In hydrothermal liquefaction process, high operating conditions cause dehydration of the biomass components. Decarboxylation is the thermal cracking of long chain carboxylic acids, which releases CO_2 and reduces the chain size. Further details on decarboxylation can be viewed in review [69]. Removal of H_2O and CO_2 from biomass gives the best option to lower oxygen contents from bio-oil since they are fully oxidized thermodynamically. Removal of H_2O from biomass produces pure carbon like substance such as charcoal while CO_2 removal from biomass tends to leave a product with high H/C ratio. A simplified concept of dehydration and decarboxylation reactions is shown in Fig. 4(a) and (b).

In hydrothermal biomass degradation, solvolysis and depolymerization are considered major reactions for bio-fuel production [72]. In solvolysis, the major role of solvent is either to fragment the

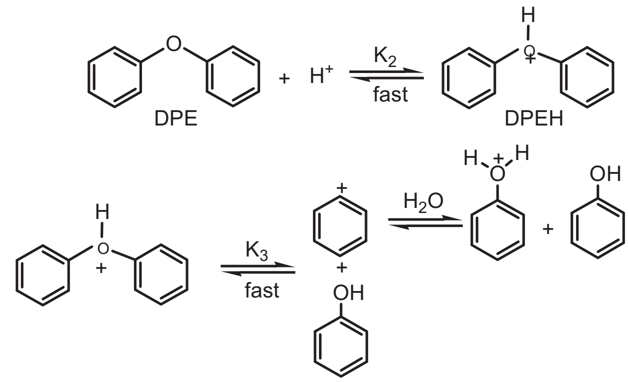


Fig. 5. Mechanism for supercritical water hydrolysis of DPE [76].

biomass by neucleophilic substitution reactions or to stabilize the fragmented products. Stabilization of biomass fragments reduces char or coke formation [73]. Hydrolysis is the term generally used when water is used as solvent for liquefaction processes. Due to high temperature, thermal breakdown of biomass also occurs during hydrolysis reactions. Hot compressed water breaks the bonds of biomass materials at heteroatom sites and hydrolyzes the fragments.

Thermal hydrolysis is different from acid or enzymatic hydrolysis. We here focus on mechanism details for thermal hydrolysis only. Many studies have searched hydrolysis pathways for hydrothermal biomass liquefaction process. Sasaki et al. [74] reported the hydrolysis of cellulose at different temperatures (320 °C, 350 °C, 400 °C) and 25 MPa. Cellulose hydrolysis was faster in supercritical or near-supercritical region in which cellulose mainly converted into aqueous oligomers (cellubiose, cellotriose, cellotetraose, cellopentaose, and cellohexaose) and monomers (glucose, fructose). Moreover, yield of hydrolysis products greatly decreased for longer residence times and vice versa for aqueous decomposition products. This suggested us the time and temperature dependency of hydrothermal degradations.

Fig. 5 explains the hydrolysis of diphenylether (DPE) by SN_1 and SN_2 mechanism under supercritical water conditions. In hydrothermal process, hydrolysis is often accompanied by thermal decomposition [75]. Under supercritical conditions, hydrolytic separation of biomass structure is followed by partial decomposition of formed compounds. Products formed by decomposition are stabilized by oxygenates or hydrogen donor species. This can cause repolymerization of fragmented compounds. Addition of hydrogen donors such as tetralin enhances the yield of liquid products. Decomposition and deoxygenation are major reactions, which produce final products containing acids, aldehydes, and aromatic compounds collectively called bio crude.

Hydrolyzed and depolymerized products usually undergo secondary reactions. Major reactions among these are condensation, dehydrations, and isomerization. Water produced during pyrolysis of biomass is mainly due to dehydration reactions.

Table 3
Effect of HD solvents and reducing gas on the yield of liquefaction products.

Feed	HD solvents	Reducing gas	Bio-oil yield (%)		Ref.
			With reducing gas or donor solvents	Without reducing gas or donor solvents	
Popular	Tetralin/THN	Air/inert	56.6	23.3	[65]
Cellulose	–	H_2/CO	38.6	5	[67]
Municipal	Tetralin	H_2	61	–	[66]
Wood	Ethyl acetate	Ar	68.4	33	[68]
Sawdust	Tetralin	–	40	–	[15]
Bituminous	Coal tar	H_2	59	48	[68]

THN, tetrahydro-naphthalene.

4.1. Degradation mechanism for cellulose in supercritical water

Cellulose is the major model compound intensively studied for the production of bio-oil since it contains 40–50% carbon and is main component of biomass [73]. References that discussed sub- and supercritical liquefaction of cellulose are available [77,78]. Cellulose is a linear chain polysaccharide of glucose monomers. In cellulose structure, glucose monomers are attached to each other via β (1-4) D-glucose units. Crystalline nature of cellulose is due to these β (1-4) linkages, which resist hydrolytic degradation by acids and enzymes [79]. However, sub- and supercritical water can break the crystallinity of cellulose by breaking inter and intra molecular hydrogen bonding. Since cellulose contains high amount of fermentable glucose, decomposition of cellulose has been studied extensively [58,80,81].

Kabyemela et al. [52] discussed mechanism of degradation of cellobiose in sub- and supercritical water. Their study-inferred cellobiose was decomposed and hydrolyzed simultaneously. Glucose and fructose were major intermediates of hydrolysis. Depolymerization yielded mainly glucosyl-erythrose (GE) and glucosyl-glycolaldehyde (GG) intermediates. Glucose and fructose intermediates were further decomposed into pyruvaldehyde, erythrose, 1,6-anhydroglucose and acids. GE and GG yielded similar products via glucose, fructose intermediates. Sinag et al. [82] reported the dependence of products composition on temperatures (325 °C, 300 °C, 375 °C) and catalysts (K_2CO_3, HZSM-5, Ni/SiO_2) during hydrothermal degradation of cellulose. The major products were glucose, fructose, 5-hydroxymethylfurfural, methylfurfural, 2-furaldehyde, acetic acid, formic acid, acetaldehyde, formaldehyde, cyclohexanon, and phenols. Carbohydrate intermediates were detected at low temperatures indicating these as hydrolyzed products of cellulose while at high temperatures no such intermediates were found. High temperature probably decomposed the intermediates into smaller products as suggested by Kabyemela et al. [52]. At near supercritical temperature acetic acids, phenols and acetaldehydes were the major products. Furfurals also behaved as secondary intermediates. The behavior of cellulose degradation is quite common in many studies [73,83]. Sakaki et al. [78] proposed saccharification and carbonization as two major steps for hydrothermal degradation of cellulose. Saccharification led formation of water-soluble sugars with minor decomposition. Saccharification was followed by carbonization that decomposed water-soluble sugars through dehydration, decarboxylation, and aromatization. As a result, water-soluble intermediates converted into gases and water insoluble products. Repolymerization of water insoluble products yielded char like solid mass. Ehara and Saka [84] compared mechanism for degradation of cellulose in supercritical water in batch type and flow type reactors. For comparison purpose, both of the reactors were operated at 380 °C, 40 MPa for 25 min duration. Cellulose was first hydrolyzed to polysaccharides with degree of polymerization in between 13 and 100. Further saccharification yielded oligosaccharides and monosaccharide (glucose and fructose). It was interesting to note that decomposed products appeared after saccharification. For both reactor types, methylglyoxal and glyceraldehydes were detected during first 10 min of operation. Further decomposition and dehydration produced erythrose, levoglycosan, 5-HMF and 5-hydroxymethyl furfural.

5. Summary

Major parameters that influence yield and composition of bio-oil are temperature, properties of solvent, solvent density, and type of biomass. Temperature is the most influencing parameter for liquid oil yield or for biomass conversion. The recommended range for final temperature may vary from 300 to 374 °C depending upon the biomass type and specifications for composition of bio oil. Temperature higher than 350 °C leads to excessive gas formation that inhibits the bio-oil production. For temperature lower than 280 °C, biomass conversion is not sufficient. Sharp temperature range 300–330 °C is advisable for cellulose, hemicelluloses, grasses, algae, and soft wood. Hardwood and lignin may need to hydrolyze at higher temperatures.

Type of solvent also affects the liquid oil yield and biomass conversion during hydrothermal extraction. Solvents support solvolysis, hydration, and pyrolysis reactions during liquefaction, which results in better fragmentation of biomass and dissolution of free radicals. Water is a suitable solvent due to its cheapness and abundant supply. Alternatively, organic solvents are also suitable options such as methanol, ethanol, acetone, tetralin, benzene, etc. Generally, extraction power of a solvent increases with increase in solvent density. This is due to the availability of extra molecules of solvents per unit molecules of biomass. For practical purposes, high solvent to biomass ratios are usually unfavorable because large amounts of solvent cost higher energy inputs and wastewater treatment problems.

Secondary parameters include residence times, heating rates, pressure, size of biomass particle, and reducing gas or hydrogen donor species. Among these, size of biomass particle and heating rates are low influencing parameters. Properties of sub/supercritical solvent nullify the effect of biomass particle size or heating rates on the yield of bio oil since supercritical solvent act both as a heat transfer medium and as an extractant during liquefaction. Solvent under sub/supercritical conditions help to overcome the heat transfer limitations that makes hydrothermal liquefaction relatively independent of the size of biomass particle or heating rates.

Residence times and reducing gases or HD solvents are moderate to low influencing parameters. At near/supercritical conditions, short residence times are usual practice in hydrothermal liquefaction. Longer residence times are more suitable in low temperature liquefaction. Once saturation point for biomass conversion is reached, further increase in residence times will be unfavorable to bio-oil yield. Effect of reducing gases is negligible on the yield of liquid oils. Low probability of reactions among the reducing gas molecules and free radicals leads to high gas or char yield. Reducing gas channeling and its maldistribution in pyrolyzing vessel are two major reasons for negligible effect of reducing gas on liquid oil yield. However, reactive gases such as CO/H_2 significantly enhance the overall yield of liquid oils. HD solvents seem to benefit bio-oil yield than reducing gases. This is due to hydrogen shuttling property of HD solvents, which maintains uniform supply of hydrogen. Tetralin is the common HD solvent for hydrothermal liquefaction processes.

Pressure also imparts low to negative effect on the yield of liquid oils in supercritical medium. The major purpose of pressure is to maintain single phase during liquefaction. However, once conditions for hydrothermal liquefaction are achieved, pressure has negligible role in modification of liquid oil yield.

Finally, the compositional variations in biomass types cause changes in composition and yield of products of liquefaction since lignin, hemicelluloses, and cellulose degraded differently during hydrothermal liquefaction. Presence of high amount of lignin contents leads to the formation of char residue. Hemicelluloses and cellulose are favorable for the bio-oil yield.

References

[1] Goyal HB, Seal D, Saxena RC. Biofuel from thermochemical conversion of renewable resources: a review. Renew Sustain Energy Rev 2008:504–17.

[2] Kelly-Yong TL, Lee KT, Mohamed AR, Bhatia S. Potential of hydrogen from oil palm biomass as a source of renewable energy worldwide. Energy Policy 2007;35:5692–701.
[3] Zmierczak WW, Miller JD. Process for catalytic conversion of lignin to liquid bio-fuels and novel bio-fuels. U.S. Patent 20,080,050,792; 2008.
[4] Jones CW, Agrawal PK. Hydrogen production from biomass. U.S. Patent 20,080,103,344; 2008.
[5] Biopower watch. Available on http://assets.panda.org/downloads/biomassreportfinal.pdf [accessed 10.09.10].
[6] Urban P. Process for converting cellulose. U.S. Patent 3,864,097; 1975.
[7] Heinz A, Kaltschmitt M, Stulpnagel R, Scheffer K. Comparison of moist vs. air-dry biomass provision chains for energy generation from annual crops. Biomass Bioenergy 2001;20:197–215.
[8] Liang T, Khan MA, Meng Q. Spatial, and temporal effects in drying biomass for energy. Biomass Bioenergy 1996;10:353–60.
[9] Wen D, Jiang H, Zhang K. Supercritical fluids technology for clean biofuel production. Prog Natural Sci 2009;19:273–84.
[10] Demirbas A. Effect of lignin content on aqueous liquefaction products of biomass. Energy Convers Manage 2000;41:1601–7.
[11] Peterson AA, Vogel F, Lachance RP, Froling M, Antal MJ, Tester JW. Thermochemical biofuel production in hydrothermal media: a review of sub- and supercritical water technologies. Energy Environ Sci 2008;1:32–65.
[12] Elliott DC, Beckman D, Bridgwater AV, Gevert SB, Solantausta Y. Developments in direct thermochemical liquefaction of biomass: 1983–1990. Energy Fuels 1991;5:399–410.
[13] Akiya N, Savage PE. Roles of water for chemical reactions in high-temperature water. Chem Rev 2002;102:2725–50.
[14] McKendry P. Energy production from biomass (part 2): conversion technologies. Bioresour Technol 2002;83:47–54.
[15] Amen-Chen C, Pakdel H, Roy C. Production of monomeric phenols by thermochemical conversion of biomass: a review. Bioresour Technol 2001;79:277–99.
[16] Savage PE, Gopalan S, Mizan TI, Martino CJ, Brock EE. Reactions at supercritical conditions: applications and fundamentals. AIChE J 1995;41:1723–78.
[17] Naik SN, Goud VV, Rout PK, Dalai AK. Production of first and second generation biofuels: a comprehensive review. Renew Sustain Energy Rev 2010;14:578–97.
[18] Effendi A, Gerhauser H, Bridgewater AV. Production of renewable phenolic resins by thermochemical conversion of biomass: a review. Renew Sustain Energy Rev 2008;12:2092–116.
[19] Guo Y, Wang SZ, Xu DH, Gong YM, Ma HH, Tang XY. Review of catalytic supercritical water gasification for hydrogen production from biomass. Renew Sustain Energy Rev 2010;14:334–43.
[20] Kucuk MM, Agirtas S. Liquefaction of *Prangmites australis* by supercritical gas extraction. Bioresour Technol 1999;69:141–3.
[21] Cagler A, Demirbas A. Conversion of cotton cocoon shell to liquid products by supercritical fluid extraction and low-pressure pyrolysis in the presence of alkalis. Energy Convers Manage 2001;42:1065–104.
[22] Cemek M, Kucuk MM. Liquid products from Verbascum stalks by supercritical fluid extraction. Energy Convers Manage 2001;42:125–30.
[23] Yuan XZ, Li H, Zeng GM, Tong TY, Xie W. Sub- and supercritical liquefaction of rice straw in the presence of ethanol–water and 2-propanol–water mixture. Energy 2007;32:2081–8.
[24] Zhong C, Wei X. A comparative experimental study on the liquefaction of wood. Energy 2004;29:1731–41.
[25] Karagoz S, Bhaskar T, Muto A, Sakata Y. Hydrothermal upgrading of biomass: effect of K_2CO_3 concentration and biomass/water ratio on products distribution. Bioresour Technol 2006;97:90–8.
[26] Sakaki T, Shibata M, Miki T, Hirosue H, Hayashi N. Reaction model of cellulose decomposition in near-critical water and fermentation of products. Bioresour Technol 1996;58:197–202.
[27] Xu C, Etchevery T. Hydro-liquefaction of woody biomass in sub and supercritical ethanol with iron-based catalysts. Fuel 2008;87:335–45.
[28] El-Rub AZ, Bramer EA, Brem G. Review of catalysts for tar elimination in biomass gasification processes. Ind Eng Chem Res 2004;43:6911–9.
[29] Yu Y, Lou X, Wu H. Some recent advances in hydrolysis of biomass in hot compressed water and its comparisons with other hydrolysis methods. Energy Fuels 2008;22:46–60.
[30] Zhou D, Zhang L, Zhang S, Fu H, Chen J. Hydrothermal liquefaction of Macroalgae *Enteromorpha prolifera* to bio-oil. Energy Fuels 2010;24:4054–61.
[31] Yin S, Dolan R, Harris M, Tan Z. Subcritical hydrothermal liquefaction of cattle manure to bio-oil: effect of conversion parameters on bio-oil yield and characterization of bio-oil. Bioresour Technol 2010;101:3657–64.
[32] Zhang B, Keitz MV, Valentas K. Thermochemical liquefaction of high-diversity grassland perennials. J Anal Appl Pyrolysis 2009;84:18–24.
[33] Sugano M, Takagi H, Hirano K, Mashimo K. Hydrothermal liquefaction of plantation biomass with two kinds of wastewater from paper industry. J Mater Sci 2008;43:2476–86.
[34] Qu Y, Wei X, Zhong C. Experimental study on the direct liquefaction of *Cunninghamia lanceolata* in water. Energy 2003;28:597–606.
[35] Xiu S, Shahbazi A, Shirley V, Cheng D. Hydrothermal pyrolysis of swine manure to bio-oil: effects of operating parameters on products yield and characterization of bio-oil. J Anal Appl Pyrolysis 2010;88:73–9.
[36] Shuping Z, Yulong W, Mingde Y, Kaleem I, Chun L, Tong J. Production and characterization of bio-oil from hydrothermal liquefaction of microalgae *Dunaliella tertiolecta cake*. Energy 2010;35:5406–11.
[37] Zhang L, Champagne P, Xu C. Bio-crude production from secondary pulp/paper-mill sludge and waste newspaper via co-liquefaction in hot compressed water. Energy 2010:1–9.
[38] Karagoz S, Bhaskar T, Muto A, Sakata Y, Azhar Uddin Md. Low-temperature hydrothermal treatment of biomass: effect of reaction parameters on products and boiling point distributions. Energy Fuels 2004;18:234–41.
[39] Mani S, Tabil LG, Sokhansanj S. Grinding performance and physical properties of wheat and barley straws, corn stover, and switchgrass. Biomass Bioenergy 2004;27:339–52.
[40] Bhaskar T, Sera A, Muto A, Sakata Y. Hydrothermal upgrading of wood biomass: influence of the addition of K_2CO_3 and cellulose/lignin ratio. Fuel 2008;87:2236–42.
[41] Srokol Z, Bouche AG, Estrik AV, Strik RCJ, Maschmeyer T, Peters JA. Hydrothermal upgrading of biomass to fuel; studies on some monosaccharide model compounds. Carbohydr Res 2004;339:1717–26.
[42] Sasaki S, Kabyemela B, Malaluan R, Hirose S, Takeda N, Adschiri T, Arai K. Cellulose hydrolysis in subcritical and supercritical water. J Supercrit Fluids 1998;13:261–8.
[43] Sasaki WM, Goto M. Recovery of phenolic compounds through the decomposition of lignin in near, and supercritical water. Chem Eng Process 2008;47:1609–19.
[44] Demirbas A. Effect of initial moisture content on the yields of oily products from pyrolysis of biomass. J Anal Appl Pyrolysis 2004;71:803–15.
[45] Sato T, Osada M, Watanabe M, Shirai M, Arai K. Gasification of alkylphenols with supported noble metal catalysts in supercritical water. Ind Eng Chem Res 2003;42:4277–82.
[46] Wang C, Pan J, Li J, Yang Z. Comparative studies of products produced from four different biomass samples via deoxy-liquefaction. Bioresour Technol 2008;99:2778–86.
[47] Boocock DGB, Sherman KM. Further aspects of powdered poplar wood liquefaction by aqueous pyrolysis. Can J Chem Eng 2009;63:627–33.
[48] Goudriaan F, Beld BVD, Boerefijn FR, Bos GM, Naber JE, Wal SVD, et al. Thermal efficiency of the THU process for biomass liquefaction, Progess in thermochemical biomass conversion, Tyrol, Austria; 2000. http://www.senternovem.nl/mmfiles/28269_tcm24-279914.pdf [accessed 10.08.10].
[49] Deshande GV, Holder GD, Shah YT. Effect of solvent density on coal liquefaction under supercritical conditions http://www.anl.gov/PCS/acsfuel/preprint%20archive/Files/30_3_CHICAGO_09-85_0112.pdf [accessed 10.08.10].
[50] Sangon S, Ratanavaraha S, Ngamprasertsith S, Prasassarakich P. Coal liquefaction using supercritical toluene–tetralin mixture in a semi-continuous reactor. Fuel Process Technol 2006;87:201–7.
[51] Kersten SRA, Potic B, Prins W, Swaaij WPMV. Gasification of model compounds and wood in hot compressed water. Ind Eng Chem Res 2006;45:4169–77.
[52] Kabyemela BM, Takigawa M, Adschiri T, Malauan RM, Arai K. Mechanism and kinetics of cellulose decomposition in sub and supercritical water. Ind Eng Chem Res 1998;37:357–61.
[53] Kabyemela MB, Adschiri T, Malaluan RM, Arai K. Kinetics of glucose epimerization and decomposition in subcritical and supercritical Water. Ind Eng Chem Res 1997;36:1552–8.
[54] Xu C, Lancaster J. Conversion of secondary pulp/paper sludge powder to liquid oil products for energy recovery by direct liquefaction in hot-compressed water. Water Res 2008;42:1571–82.
[55] Hai-feng Z, Xiao-li S, Dong-kai S, Rong Z, Ji-Cheng B. Investigation on degradation of polyethylene to oil in a continuous supercritical water reactor. J Fuel Chem Technol 2007;35:487–91.
[56] Xiaoli S, Zhao Y, Zhang R, Bi J. Investigation on degradation of polyethylene oils in supercritical water. Fuel Process Technol 2004;85:1249–58.
[57] Yan Y, Xu J, Li T, Ren. Liquefaction of sawdust for liquid fuel. Fuel Process Technol 1999;60:135–43.
[58] Sasaki M, Adschiri T, Arai K. Production of cellulose II from native cellulose by near and supercritical water solubilization. J Agric Food Chem 2003;51:5376–81.
[59] Loppinet-Serani A, Aymonier C, Cansell F. Current and foreseeable applications of supercritical water for energy and the environment. Chem Sus Chem 2008;1:486–503.
[60] Wang G, Li W, Li B, Chen H. Direct liquefaction of sawdust under syngas. Fuel 2007;86:1587–93.
[61] Neavel RC, Knights CF, Schulz H. Donor solvent liquefaction process. Math Phys Sci 1981;300:141–56.
[62] Li H, Yuan X, Zeng G, Tong J, Yan Y, et al. Liquefaction of rice straw in sub and supercritical 1,4-dioxane-water mixture. Fuel Process Technol 2009;90:657–63.
[63] Bestue-Labazuy C, Soyer N, Bruneau C, Brault A. Wood liquefaction with hydrogen or helium in the presence of iron additives. Can J Chem Eng 2009;63:634–8.
[64] Akhtar J, Kuang SK, Amin NAS. Liquefaction of empty palm fruit bunch (EPFB) in alkaline hot compressed water. Renew Energy 2010;35:1220–7.
[65] Phillips CR, Granatstein DL. Production of hydrocarbon liquids from solid carbonaceous materials. C.A. Patent 1,100,532; 1981.
[66] Benn FR, McAuliffe CA. Conversion of a municipal waste to fuel. U.S. Patent 46,187,361,986.
[67] Shinya Y, Tomoko O, Katsuya O. Liquefaction of wooden biomass. J.P. Patent 60,262,888; 1985.
[68] Silvestri AJ, Naro PA. Liquefaction of coal. U.S. Patent 3,923,634; 1975.

[69] Zhengang L, Fu-Shen Z. Effects of various solvents on the liquefaction of biomass to produce fuels and chemical feedstock. Energy Convers Manage 2008;49:3489–504.
[70] Asghari FS, Yoshida H. Dehydration of fructose to 5-hydroxymethylfurfural in sub-critical water over heterogeneous zirconium phosphate catalysts. Carbohydr Res 2006;341:2379–87.
[71] Snare M, Kubickova I, Maki-Arvela P, Eranen K, Warna J, Murzin DY. Production of diesel fuel from renewable feeds: kinetics of ethyl stearate decarboxylation. Chem Eng J 2007;134:29–34.
[72] Behrendt F, Neubauer Y, Oevermann M, Wilmes B, Zobel N. Direct liquefaction of biomass: review. Chem Eng Technol 2008;31:667.
[73] Jakab E, Liu K, Meuzelaar HLC. Thermal decomposition of wood and cellulose in the presence of solvent vapors. Ind Eng Chem Res 1997;36:2087–95.
[74] Sasaki M, Fang Z, Fukushima Y, Adschiri T, Arai K. Dissolution and hydrolysis of cellulose in subcritical and supercritical water. Ind Eng Chem Res 2000;39:2883–90.
[75] Minowa T, Fang Z, Ogi T, Varhegyi G. Decomposition of cellulose and glucose in hot-compressed water under catalyst-free conditions. J Chem Eng Jpn 1998;31:131–4.
[76] Penninger JML, Kersten RJA, Baur HCL. Reactions of diphenylether in supercritical water-mechanism and kinetics. J Supercrit Fluids 1999;16:119–32.
[77] Kamio E, Takahashi S, Noda H, Fukuhara C, Okamura T. Effect of heating rate on liquefaction of cellulose by hot compressed water. Chem Eng J 2008;137:328–38.
[78] Sakaki T, Shibata M, Miki T, Hirosue H. Decomposition of cellulose in near critical. Energy Fuels 1996;10:684–8.
[79] Puri VP. Effect of crystallinity and degree of polymerization of cellulose on enzymatic saccharification. Biotechnol Bioengin 1984;26:1219–22.
[80] Ishikawa Y, Saka S. Chemical conversion of cellulose as treated in supercritical methanol. Cellulose 2001;8:189–95.
[81] Saka S, Ueno T. Chemical conversion of various cellulose to glucose and its derivatives in supercritical water. Cellulose 1999;6:177–91.
[82] Sinag A, Gulbay S, Uskan B, Gullu M. Comparative studies of intermediates produced from hydrothermal treatments of sawdust and cellulose. J Supercrit Fluids 2009;50:121–7.
[83] Kumar S, Gupta RB. Hydrolysis of microcrystalline cellulose in subcritical and supercritical water in a continuous flow reactor. Ind Eng Chem Res 2008;47:9321–9.
[84] Ehara K, Saka S. A comparative study on chemical conversion of cellulose between the batch-type and flow-type system in supercritical water. Cellulose 2002;9:301–11.